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Bond dissociation and internal energies of the gas phase $TiCl_n^+$ ions formed by 70 eV electron impact ionization: an ion beam study

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Abstract

An ion beam instrument has been constructed that utilizes a unique, simple ion deceleration lens. We demonstrate here that the kinetic energies of the ions formed can be determined accurately and precisely over a range of energies, that endothermic processes can be characterized, and that the instrument exhibits high product ion collection efficiencies. Results of collision-induced dissociation studies of the $TiCl_n^+$ ions ($n = 1–4$), generated by 70 eV electron impact ionization, are presented here. The results are compared with those obtained from threshold measurements, and indicate that these ions are formed with substantial average internal energies. This information is useful, since the rich gas phase chemistry of $TiCl_n^+$ ions with organic molecules reported to date involves reactant ions that have not been thermalized. (Int J Mass Spectrom 182/183 (1999) 163–173) © 1999 Elsevier Science B.V.

Keywords: Chlorotitanium ions; Collision-induced dissociation

1. Introduction

It has been more than 20 years since the first report of the formation of a metal–carbon bond in a gas phase ion/molecule reaction [1]. Early studies of gas phase organometallic chemistry involving metal ions [2–4] used electron impact on volatile metal-containing compounds to generate atomic ions such as Fe^+, Ni^+, and Co^+, as well as a variety of ligated metal ions, ML_n^+, such as $CoNO^+$, $Fe(CO)_{1–5}^+$, and $NiC_5H_5^+$ [5]. Of the various ML_n^+ systems studied, the $TiCl_n^+$ ions exhibit some of the richest chemistry, which undergoes distinct changes as n is varied [6–8]. The Ti^+ and the $TiCl_{1–4}^+$ ions were generated by 70 eV electron impact ionization (EI), and were allowed to react with neutral organic molecules at low pressure in the gas phase. The products of these reactions were characterized by ion cyclotron resonance mass spectrometry (ICR MS). Electron impact and thermionic emissions were the only tools available to generate gas phase metal ions until Ben Freiser developed laser-based methods to use with ICR MS [9].

While the possibility of excited state chemistry

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Dedicated to the memory of Ben Freiser to commemorate his many seminal contributions to mass spectrometry and gas phase ion chemistry.

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was considered when metal-containing gas phase ions were generated by EI [10], the reactions did not appear to depend on the ionizing electron energy. Since these early studies, elegant approaches and instrumentation have been developed for thermalizing excited atomic ions [11–13], and small metal-containing molecular ions [14], formed in a variety of ways [15–17], for subsequent ion/molecule studies. Also, ion beam methods [13,18], Fourier transform ion cyclotron resonance (FTICR) spectrometry [19], and triple quadrupole mass spectrometry (TQMS) [12,20] techniques were developed for studying not only exothermic, but endothermic processes as well. One of the earliest systems studied was the chemistry of atomic, first-row transition metal ions with small organic halides such as CH_3I and CH_3Br [1,21,22]. More sophisticated experiments have subsequently shown that the chemistry observed was influenced by the excited states of the atomic metal ions generated by EI [23].

Were the reactions reported for the $TiCl_n^+$ ions with alkenes and oxygen-containing organic compounds influenced by excited states/excess internal energy of the EI-formed ions? This question is relevant since the study of the chemistry of these ions continues to yield intriguing results [24]. Although insights into excited state populations of atomic metal ions formed by EI have been developed, little is known for ligated metal ions such as these. One way to begin to address this question is to attempt to thermalize the ions prior to their interaction with neutral partners and to determine differences in the chemistry. Another approach, which we use here, is to investigate directly the internal energy content of the chlorotitanium ions formed by EI. Ion beam experiments were performed on an instrument described in sec. 2, which utilizes a relatively simple ion deceleration lens system that was developed in this laboratory. Collision-induced dissociation (CID) thresholds for the $TiCl_n^+$ ions ($n = 1$–4) formed by EI of $TiCl_4$(g) have been determined. Results are compared with previously proposed bond-dissociation energies (BDEs) extracted from appearance potential measurements for these ions [25]. The BDEs determined by CID are not the same as those reported for, presumably, ground-state species. The differences between these two measurements suggest limits on the internal energy contents of these EI-formed ions.

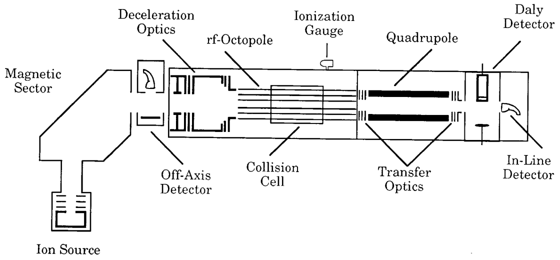


Fig. 1. Ion beam instrument schematic diagram.

2. Experimental

Instrumentation used for the measurements presented here has been described previously [26]. An important modification was made to reduce the energy spread of the mass selected cations. The MSU ion beam instrument was developed using a Varian MAT CH5 double-focusing mass spectrometer at the “front end” to generate 1000 eV mass-selected ions. The reverse geometry (BE) design provided good spatial focusing, but contributed to the energy spread of the mass-selected ions that are generated by the instrument. Thus, the electric sector was removed, and mass selection was accomplished with the magnetic sector alone. When the electric sector was present, the kinetic energy spread of the ion beam was 0.31 ± 0.02 eV; with the electric sector removed, the spread was reduced to 0.25 ± 0.02 eV. A schematic representation of the instrument is provided in Fig. 1.

Ions were generated using an Intensitron EI source, which was part of the Varian MAT CH5 mass spectrometer. Manufacturer’s literature states the “saddle-field” potential energy surface within the source produces an ion beam with a kinetic energy spread of approximately 0.3 eV. After the ions are generated and extracted from the source, they are accelerated to approximately 1000 eV and focused into a 90° magnetic sector where they are separated on the basis of their momenta. Upon exiting the magnet, the ions are refocused and their kinetic energies are reduced by deceleration optics. Details of the development of the deceleration optics have been reported previously [26]. After the kinetic energy of the ions has been established, they are injected into an rf-only octopole ion beam guide. The beam guide passes through a collision cell where the ions undergo collisions with a neutral reagent gas. Transfer optics focus the product ions and unreacted primary ions exiting the octopole, and inject them into a quadrupole mass filter, which provides mass to charge ratio analysis. Detection of the ions is performed by employing a Daly-type scintillation detector and using standard pulse-counting techniques. Cations impinge on a 1.25 in. diameter stainless-steel target, maintained at a potential of −27 kV. The resulting, sputtered electrons fall through a 27 kV potential and strike a plastic scintillator, which is optically coupled to a Hamamatsu R-425 photomultiplier tube (PMT). Each ion collision with the stainless-steel conversion dynode results in a 50 ns pulse from the PMT. When the amplitude of this pulse is greater than a selected threshold, it is converted into a transistor–transistor logic (TTL) pulse, which is sent to pulse-counting electronics.

To improve the precision and accuracy of the pressure measurements of the collision cell, an ionization gauge (mounted on the side of the chamber which houses the beam guide and collision cell), calibrated against a capacitance manometer, was employed. Calibration was performed under molecular flow conditions to assure a linear pressure drop from the collision cell. A calibration curve was generated for each neutral reagent gas.

Energies in the laboratory frame (lab) were converted to the center-of-mass frame. The full width at half maximum (FWHM) of the kinetic energy distribution of the ions, as well as the absolute energy scale, were determined by using the octopole as a retarding energy analyzer [26]. Absolute uncertainty in the energy scale has been determined to be ±0.05 eV [26]. The kinetic energy distribution was nearly Gaussian in shape with FWHM values typically in the range of 0.2–0.4 eV.

Total reaction cross sections, σ, are calculated using

$$I_r = (I_r + \sum I_i) \exp(-n\sigma l) \tag{1}$$

where n is the number density of the neutral gas, l is the effective collision cell length, I_r is the measured intensity of the transmitted reactant ion beam, and I_i refers to specific product ion signals.

The energy-dependent reaction cross section, $\sigma(E)$, was modeled near the threshold region by

$$\sigma(E) = \sigma_o(E - E_T)^n/E^m \tag{2}$$

where E is the kinetic energy available to the system, E_T is the energy of the threshold, n and m are adjustable parameters, and σ_o is an energy-independent scaling factor [27]. Reasonable values for E_T were generated only when m was not allowed to vary and was set equal to 1. Convolution of the data was accomplished by first fitting, through a least-squares routine, the steepest, straightest section of the curve. After obtaining the best fit, a curve, based on the newly acquired parameters, was drawn from a point below the threshold to the point of maximum kinetic energy of the region best fit. Convolution of the data was performed using software developed by the Armentrout group, CRUNCH [28].

Instrument evaluation. Data from two experiments are provided to demonstrate the quality of the measurements made with the MSU ion beam instrument. The first involved the determination of the BDE of Mn_2^+, and illustrates the energy accuracy and precision of the instrument. The second experiment was a study of the energy dependence of the gas-phase reaction between Ar^+ and molecular deuterium. This investigation demonstrated the product collection efficiency of the instrument.

CID of Mn_2^+. To demonstrate that the MSU ion beam instrument can be used to obtain reproducible and accurate relative reaction cross-section measurements for endothermic processes, CID experiments were carried out to determine the metal–metal bond energy of the singly charged manganese dimer ion, previously reported by Armentrout and co-workers [27]. The CID experiment was conducted using argon as the collision gas and is represented as

$$Mn_2^+ + Ar \rightarrow Mn^+ + Mn + Ar$$

$$\Delta H = 0.85 \pm 0.2 \text{ eV} \tag{3}$$

The primary reactant ions, Mn_2^+, were generated by electron impact ionization of $Mn_2(CO)_{10}(g)$. A direct insertion probe was used to introduce the solid $Mn_2(CO)_{10}$ into the ionization chamber; a primary ion beam with a current corresponding to 1.0×10^6 ions/s was generated. To limit the excess internal energy in the precursor ion, 18.5 eV electrons were used, rather than the normal 70 eV electron bombardment energy. Calibration of the electron energy was performed using molecular nitrogen by scanning the electron energy, generating a clastogram (plot of relative mass spectral peak intensities versus electron energy), determining the IE of N_2, and comparing it with the known value.

With no gas introduced into the collision cell, the base pressure of the instrument is approximately 2.1×10^{-7} Torr. (The pressure is monitored by the ionization gauge mounted on the vacuum chamber containing the octopole and collision cell. The gauge was calibrated for argon.) A stopping potential experiment was performed in which the primary ion beam energy was varied by sweeping the octopole (dc) bias through the acceleration potential while the quadrupole was operated in the rf-only mode. The primary ion beam kinetic energy spread was calculated to be 0.27 ± .02 eV, as determined from repeated stopping potential curves.

For the CID experiments, high purity Ar (99.999%, AGA Gas Inc.) was used as the collision gas. Pressure within the collision cell was maintained at 0.09 mTorr. The background pressure of the chamber was measured to be 6.4×10^{-6} Torr. The cross section for the CID process was measured for collision energies from 1 to 21 eV in the laboratory frame. A background scan (no gas in the collision cell) was performed for each CID experiment with each pair of scans performed in triplicate. Each background scan was subtracted from its corresponding CID scan. Because of this background subtraction, some of the relative cross-section values below the CID threshold are slightly negative. These negative values have been set equal to zero. The results of one experiment are shown in Fig. 2(A).

Precision of the instrument is illustrated when the results of the three experiments are plotted together, as shown in Fig. 2(B). Based on data generated from Mn_2^+ ions formed by ~18 eV EI, through curve-fitting and deconvolution, Armentrout and co-workers [27] determined the Mn_2^+ bond dissociation energy, BDE(Mn_2^+), to be 0.85 ± 0.2 eV. The fits to our data for three experiments lead to a BDE of 0.91 ± 0.1 eV.

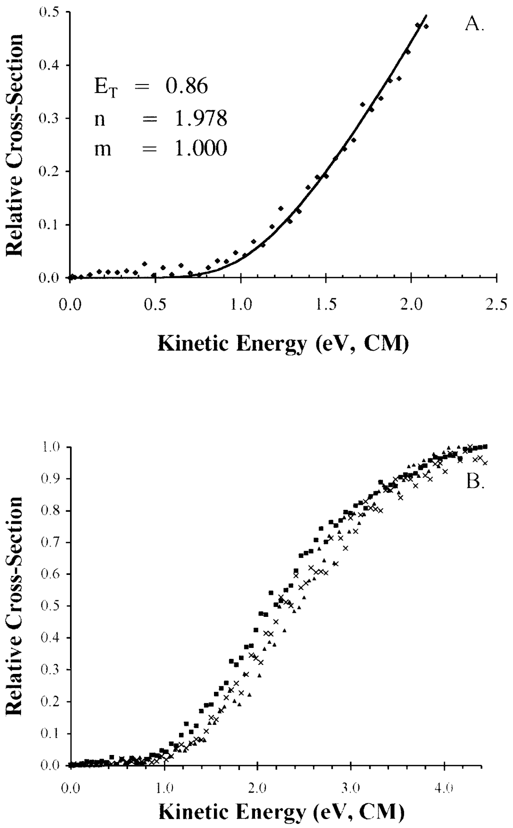


Fig. 2. CID results for $Mn_2^+ + Ar \rightarrow Mn^+ + Mn + Ar$. (A) Experimental results and the curve of best fit. The parameters n, m, and E_T are defined in the text. (B) Comparison of three data sets to illustrate the reproducibility of the experiment.

The Mn_2^+ CID experiments demonstrate that the MSU ion beam instrument can be used to generate reproducible and accurate relative cross-section measurements for endothermic processes involving ions generated through electron-impact ionization.

$Ar^+ + D_2$. The hydrogen atom transfer reaction to singly charged argon from molecular hydrogen and its isotopic counterpart, molecular deuterium, has been extensively studied to the point that it “represents one of the most thoroughly investigated systems in the

history of ion–molecule chemistry" [18]. The following reaction has been found to be exothermic by 1.50 eV for ground state reactants and products:

$$Ar^+ + D_2 \rightarrow ArD^+ + D$$

$$\Delta H = -1.50 \pm 0.03 \text{ eV} \tag{4}$$

Energy dependent cross sections for exothermic reactions are at their maximum at or near the lowest translational energies. Also, because of the release of excess energy, products may possess high translational energies. These two factors contribute to a high degree of scattering in the collision cell of both the reactant and product ions. Because of this scattering, there is a great deal of difficulty in performing these types of experiments in a longitudinal ion beam instrument [18]. The well-studied $Ar^+ + D_2$ system is thus useful for evaluating the performance of the MSU ion beam instrument.

Argon ions were generated by 70 eV electron impact ionization. Primary ion currents of 2.5×10^6 ions/s were obtained. With the collision cell maintained at its base pressure of 2.5×10^{-7} Torr, as measured by the ionization gauge, stopping potential analyses were performed. The quadrupole was operated in the rf-only mode. The primary ion beam kinetic energy spread was calculated to be 0.29 ± 0.02 eV, as determined from three separate stopping potential curves.

Technical grade deuterium (AGA Gas, Inc.) was used for the energy-resolved reaction studies. The pressure within the collision cell was maintained at 0.09 mTorr as measured by the ionization gauge calibrated for deuterium. The background pressure of the chamber was measured to be 6.2×10^{-6} Torr. The reactions were monitored for ion kinetic energies from 1 to 9.5 eV in the laboratory frame. To achieve the highest ion beam current, the quadrupole was operated with the lowest resolution that completely separated the primary reactant ions from the product ions.

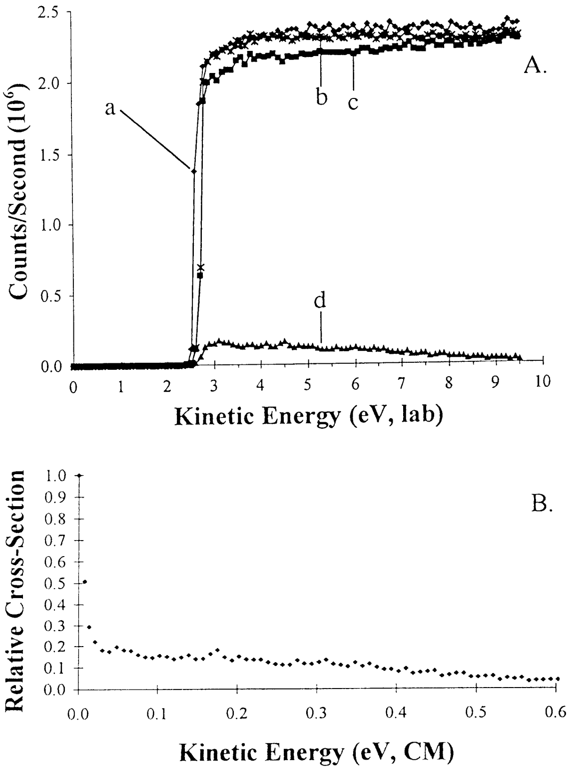


Fig. 3. Experimental results from the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$. (A) Illustration of the collection efficiency of the MSU instrument. Because of the "saddle-field" potential energy surface within the source, reactant ions are generated at a potential below the potential applied to the source housing (V_{accel}). This means that ions will not be injected into the collision cell until the static dc potential of the octopole is equivalent to the actual potential at which the ions were formed. In this case, the ions were formed at a potential approximately 2.5 V below the potential applied to the source housing. Data are shown for (A) Ar^+ with no D_2 in the collision cell; (B) the sum of Ar^+ and ArD^+ with D_2 in the collision cell; (C) Ar^+ with D_2 in the collision cell; and (D) ArD^+, with D_2 in the collision cell. (b) Energy dependence of the relative reaction cross section.

Results of the experiments are shown in Fig. 3(A) and (B). Stopping potential experiments were performed by monitoring the primary argon ion current as a function of kinetic energy with no gas introduced into the collision cell. Deuterium was then introduced into the collision cell. The reactant ion, Ar^+, and product ion, ArD^+, were then monitored as a function of Ar^+ kinetic energy. A background scan was then taken. Each scan was performed in triplicate. As shown in Fig. 3(A), the sum of the transmitted ion beam current and the product ion current is almost equal to the primary ion intensity when no gas was present in the collision cell.

The data were collected and converted to the center-of-mass frame as described. The energy-dependent relative reaction cross-section is shown in Fig. 3(B). The curve is an average of three separate experiments. The data compare well to those reported by Ervin and Armentrout [18]. As expected, the cross section is at a maximum at the lowest interaction energy and decreases exponentially as the energy is increased.

Measurements of the reaction between singly charged argon ions and molecular deuterium demonstrate that high trapping and transmission efficiencies for highly scattered reactant and product ions of exothermic ion–molecule reactions are attainable, even at low interaction energies, with the MSU ion beam instrument. These experiments demonstrate that the ion source/magnetic sector/octopole collision cell/quadrupole mass filter combination interfaces well to the deceleration lens that we have developed.

CID of the $TiCl_n^+$ *ions.* Experiments were performed by applying a nominal potential of 1000 V (V_{accel}) to the ion source. Ions were generated by 70 eV EI on $TiCl_4$ (99.9% pure, Aldrich). The 70 eV mass spectrum of $TiCl_4$ consists of Ti^+ (3.4%), $TiCl^+$ (6.2%), $TiCl_2^+$ (11.5%), $TiCl_3^+$ (45.7%), and $TiCl_4^+$ (33.2%) [6]. For the CID experiments, high purity Ar (99.999%, AGA Gas, Inc.) was used as the collision gas. The octopole was swept from +5 V to −35 V relative to V_{accel} and the static dc offset of the quadrupole was set to −30 V relative to V_{accel}. Pressure in the collision cell was maintained at 8×10^{-5} Torr. The base pressure of the instrument was typically 4×10^{-7} Torr.

3. Results and discussion

We present here direct measurements of the bond dissociation energies of the $TiCl_n^+$ ions formed by 70 eV EI of $TiCl_4$. Thermochemical data for these ions have been extracted from previous measurements. Kiser, Dillard, and Dugger (KDD) performed ionization and appearance energy experiments to determine the heats of formation for the positive ions generated from titanium tetrachloride [25]. Ionization efficiency curves were evaluated by the semilogarithmic plot technique described by Lossing, Tickner, and Bryce [29]. Appearance potentials were then extrapolated from the data using a procedure outlined by Warren [30], and from these, enthalpies of formation were extracted. The KDD results are listed in Table 1. Bond dissociation energies (BDEs) were calculated from information in the article, and using $\Delta H_f^o(\mathrm{Cl})(\mathrm{g}) = 29.0$ kcal/mol and $\Delta H_f^o(\mathrm{TiCl_4})(\mathrm{g}) = -182$ kcal/mol [31]. These BDEs are also presented in Table 1.

Table 1
Calculated thermochemical data for ions produced from $TiCl_4$

Ion	ΔH_f^o (ion)[a] (kcal/mol)	BDE[b] (kcal/mol)
$TiCl_3^+$—Cl	87	38
$TiCl_2^+$—Cl	96	78
$TiCl^+$—Cl	145	90
Ti^+—Cl	206	102
Ti^+	279	

[a] See [25].
[b] Computed as described in text.

Appearance energy (AE) measurements have historically been powerful tools for establishing gas phase ion and neutral thermochemistry. They can be influenced by kinetic and competitive shifts [32], and may be higher than the true minimum energy required for a particular process. Thus, ionic heats of formation measured in this way should be considered as upper limits to actual values.

Are the BDEs listed in Table 1 reasonable and could they represent ground state values? Certainly their magnitudes are not unreasonable. KDD considered, and rejected, fragmentation mechanisms involving ion pair formation, as well as the elimination of molecular chlorine as opposed to two Cl atoms when forming fragment ions such as $TiCl_2^+$. The BDEs increase as the number of chlorine atoms in the ions decrease. This is somewhat different from values reported for similar systems. Consider the CCl_n^+ ions, whose BDEs are listed in Table 2. The molecular ion of CCl_4 has not been observed, presumably because of the small BDE(CCl_3^+–Cl). The BDEs alternate between strong and weak values as the number of chlorine atoms attached to the central atom varies, as illustrated in Table 2. The same is true for the $SiCl_n^+$ ions from $SiCl_4$ and the CF_n^+ ions from CF_4. (CF_4 is another example of a compound for which a molec-

Table 2
Bond dissociation energies (BDEs) for similar systems (all values in kcal/mol)[a]

Bond	Precursor (MX_4) CCl_4	$SiCl_4$	CF_4	CH_4
MX_3^+—X	—	14	—	42
MX_2^+—X	108	116	138	122
MX^+—X	48	46	76	108
M^+—X	163	122	179	95

[a] BDEs were calculated from heats of formation provided in [31].

ular ion is not observed in EI mass spectrometry.) In contrast, the relationship between BDE and number of atoms attached to the central atom is very different for the CH_n^+ ions derived from CH_4; this is not unexpected. In an ion such as CCl_3^+, the C–Cl bond order is greater than 1, in part due to Cl → C backbonding, involving a lone pair on the Cl and an empty *p* orbital on the charged central atom [33]. This obviously is not an option for CH_3^+.

Considering errors inherent in making AP measurements, and how they can accumulate when measuring values other than an ionization energy of the first fragment ion, one might expect the largest error to exist in KDD's data for Ti^+ from $TiCl_4$. Yet, their $\Delta H_f(Ti^+)$ of 279 ± 7 kcal/mol compares well with a more recently [31] determined value of 269.5 kcal/mol. We will, at this point, accept the KDD data as providing reasonable ground state BDEs for these ions, and use them as the starting point for evaluating our results.

CID of $TiCl_n^+$ ions. Fig. 4(A) shows the results of a CID experiment on $TiCl^+$ with argon as the neutral target gas. As the ion kinetic energy is increased, the cross section for dissociation to Ti^+ increases. The best fit of Eq. (2) to the data was obtained by setting $m = 1$ and allowing n to vary. The cross-section function has been plotted relative to the maximum cross section over the region of data shown. The filled squares represent the experimental results, the Ti^+ signal, and the solid line shows the best fit using Eq. (2). As seen from Fig. 4(A), there is a good fit to the data from about 4 eV to the high energy end of the plot. There is clearly some noise/structure in the low energy region. However, several data sets for this system yield the same values when the data points are fit to Eq. (2), yielding a value for the BDE(Ti^+–Cl), generated by 70 eV EI, of 64 ± 7 kcal/mol. Figs. 4(B) and 5 show plots resulting from the CID experiments for $TiCl_n^+ (n = 2–4)$. In each case, there is a good correlation between the data and the curve shown for the values of n, m, and E_T indicated.

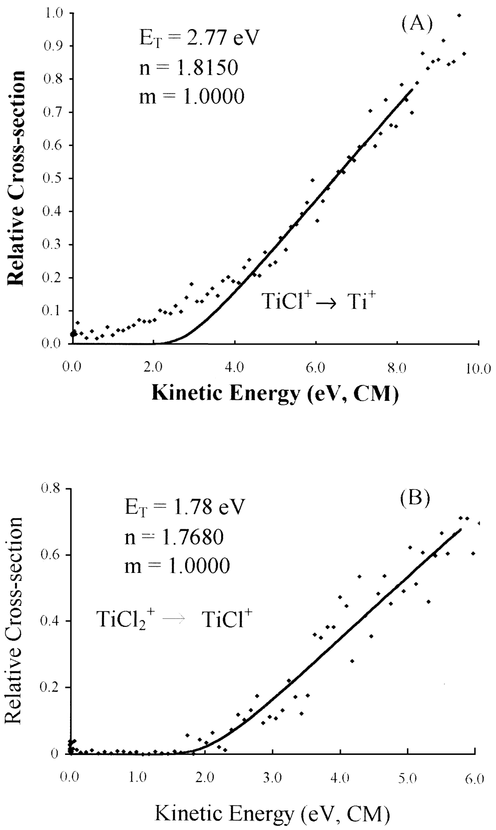


Fig. 4. (A) Relative energy-dependent cross section for CID of $TiCl^+$. (B) Relative energy-dependent cross section for CID of $TiCl_2^+$. Argon was used as the collision gas during both experiments.

The BDEs for $TiCl_2^+$, $TiCl_3^+$, and $TiCl_4^+$, obtained from multiple measurements similar to those presented here, are 41 ± 2, 65 ± 10, and 8 ± 2 kcal/mol, respectively. The large relative uncertainty in the BDE($TiCl_3^+$–Cl) arises from the threshold having a value so close to the zero kinetic energy point.

A comparison of these results to those of KDD is given in Fig. 6. The BDEs determined as described are substantially different, with the values determined in this work always being smaller than the KDD data

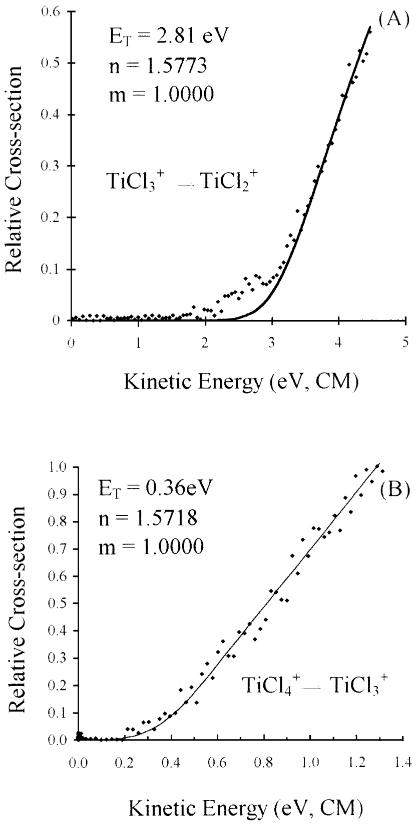


Fig. 5 (A) Relative energy-dependent cross section for CID of $TiCl_3^+$. (B) Relative energy-dependent cross section for CID of $TiCl_4^+$. Argon was used as the collision gas during both experiments.

set. One interpretation, which will be considered here, is that both are correct, and that the differences between the CID data presented here and the KDD threshold measurements reflect average internal energy content in the ions generated by 70 eV electron impact.

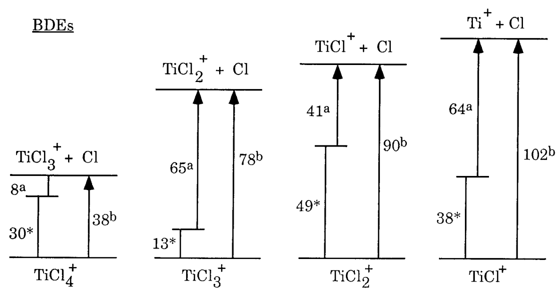


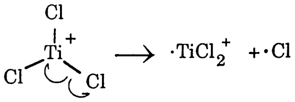
Fig. 6. Differences in BDEs between this study (a) and a previous study (b). [25] (*) denotes the difference between each set. All values are in kcal/mol.

The chemistry of the $TiCl_n^+$ ions with acetone molecules has been previously reported [6]. Among the chlorotitanium ions, acetone will displace a chlorine atom only from $TiCl_4^+$. The $TiCl_{2,3}^+$ ions react by HCl elimination. The $TiCl^+$ ion reacts, but not by losing its Cl atom. These observations would be consistent with the KDD data, with BDEs increasing as n increases; however, other variables could determine these changes in reactivity as well. A more detailed analysis of the results for each of the chlorotitanium ions follows.

$TiCl_4^+$. As shown in Fig. 6, if the KDD results and those presented here are both correct, then the $TiCl_4^+$ ions formed by 70 eV EI have average internal energies of approximately 30 kcal/mol, only slightly less than the BDE($TiCl_3^+$–Cl) of 38 kcal/mol. From an energetic standpoint, this is not unreasonable. Most of the $TiCl_4^+$ ions formed in EI (70 eV) dissociate [6], with $TiCl_3^+$ being the most abundant fragment ion. If $TiCl_4^+$ is the precursor to all $TiCl_n^+ (n = 0–3)$ ions, the 70 eV EI mass spectrum of $TiCl_4$ shows that only 33.2% of the $TiCl_4^+$ ions formed remain intact. Thus, most likely more than 38 kcal/mol is deposited into the molecular ion during the ionization process. Those ions with more than 38 kcal/mol of internal energy fragment; those with internal energies less than the BDE cannot fragment and are the ions whose chemistry has been characterized (and studied here). The very small *apparent* BDE, 8 kcal/mol, is consistent with the observation that neutral oxygen-containing organic molecules can only displace a Cl atom in $TiCl_4^+$ ions at thermal collision energies [6]. Presumably, weakly bound ion–dipole complexes are formed. This observation could also be due to the fact that, of the $TiCl_n^+$ ions, only $TiCl_4^+$ has no low-lying empty orbitals that can interact with organic molecules and form bonds, so ligand displacement is one of the few chemical options it has.

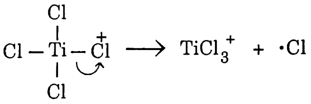
When $TiCl_4$ is ionized, the lowest energy process involves removal of an electron from a chlorine atom [34]. Thus, of the $TiCl_n^+$ ions, the positive charge may reside on the metal in all cases except when $n = 4$.

For example, when $TiCl_3^+$ dissociates, it can undergo a homolytic bond cleavage, reaction (5). In the simplest model, charge resides on the metal in both reactant and product



(5)

However, bond cleavage in $TiCl_4^+$ is ultimately heterolytic; reaction (6)



(6)

is equivalent to a homolytic cleavage followed by charge transfer. While the chlorine holds the charge in $TiCl_4^+$, as the bond breaks, the IE(Cl), 13 eV, is high compared with that for the $TiCl_3$ fragment it leaves behind, 9.7 eV. The fragmentation of $TiCl_4^+$ via a heterolytic process may be unique for the chlorotitanium ions and may influence the observed BDE.

It is worthy to note that the condensed phase chemistry of $TiCl_4$ is different from that observed for $TiCl_4^+$ [8]. $TiCl_4$ reacts with a variety of molecules, RH, to form $\{TiCl_3R + HCl\}$ and $\{TiCl_2R_2 + 2HCl\}$. $TiCl_4^+$ is largely unreactive, except with some polar molecules, with which it reacts via Cl atom displacement. Certainly the presence and location of the charge have a substantial chemical consequence, and the observed chemistry is consistent with a low BDE($TiCl_3^+$–Cl).

$TiCl_3^+$. Approximately 30% of the $TiCl_3^+$ ions formed in the 70 eV EI process dissociate further [6]; if the energy required to cleave a Ti–Cl bond in this ion is 78 kcal/mol, then those $TiCl_3^+$ cations with internal energies in the 0–77 kcal/mol range will remain intact. Thus, a mean internal energy for this ion of 13 kcal/mol, as suggested by the difference in BDEs between this study and KDD, is certainly plausible. If $TiCl_4^+$ loses a $Cl^{\cdot}$ atom, the resulting $TiCl_3^+$ ion is an even electron species. An electron pair on a Cl atom can backdonate to an empty *p* orbital on the metal to form a dative bond, giving an overall Ti–Cl bond order in $TiCl_3^+$ of 1.3. The resulting ground state structure would be planar. Certainly the bonding is not this simple. When a titanium ion and a chlorine atom are brought together to form a bond, electrons flow between the metal and ligand in both the σ and π systems, yielding the stable bond. In addition to the possibility of dative bonding in the π system, electrons flow in the σ system from the metal to the ligand. To the extent such bonding has ionic character, with a net flow of electrons away from the metal, this would also result in shorter bonds and a change in geometry. If the ground states of $TiCl_4$ and $TiCl_4^+$ are tetrahedral, the ionization process is a vertical transition, and dissociation is prompt, then the nascent $TiCl_3^+$ ion would be pyramidal, with longer bonds than in the ground state of the ion, resulting in a vibrationally excited species. Prompt fragmentation following ionization is most likely when ionization energies substantially above threshold are used, and when the parent molecule is small with few degrees of freedom [32,35]. Certainly for the first fragment ion this simple bond cleavage can be prompt following ionization, as opposed to more complex rearrangement reactions that can be observed in mass spectrometry. A geometric mismatch between a fragment ion and its immediate precursor is not a necessary condition for the formation of vibrationally "hot" ions. Fragment ions can be formed with excess internal energy following 70 eV ionization, particularly in cases like $TiCl_3^+$ where the neutral lost is atomic, having no vibrational degrees of freedom [36–38].

$TiCl_2^+$. The same considerations can be applied to the other fragment ions. Approximately half of the $TiCl_2^+$ ions formed by 70 eV ionization of $TiCl_4$ dissociate further [6], so they can be formed with internal energies greater than 90 kcal/mol, if the KDD value for the BDE($TiCl^+$–Cl) is correct. The ground state of the radical ion $TiCl_2^+$ is expected of have a Cl–Ti–Cl bond angle greater than that of its precursor, and a bond order of 1.5 if dative bonding in the π system were operative. At the other extreme, if the bonding is substantially ionic, with negative charge generated on the Cl atoms, this would also result in shorter bonds and a change in geometry. Thus, generation of vibrationally excited $TiCl_2^+$ ions from $TiCl_4$, via $TiCl_3^+$, is not unexpected.

$TiCl^+$. If the EI process first involves the formation of the molecular ion of the precursor, and all

fragment ions rapidly evolve from the molecular ion, it may be unexpected that excess energy would remain after three Ti–Cl bonds are cleaved. Nonetheless, a third of the $TiCl^+$ ions formed from $TiCl_4$ further dissociate to $\{Ti^+ + Cl\}$ [6], and are thus formed with internal energies exceeding the BDE. In this light, an average internal energy of 38 kcal/mol as suggested by Fig. 6 is not unreasonable. Again, the expected geometric mismatch, between the relatively short Ti–Cl bond in the diatomic cation versus the neutral precursor and its immediate precursor, $TiCl_2^+$, would be consistent with the formation of vibrationally excited fragment ions.

Ti^+. Atomic ions, Ti^+, are also formed by electron impact on $TiCl_4$, although in low relative abundance [6]. It is noteworthy that these ions are also formed with excess internal energy, here in the form of electronic excitation. Kemper and Bowers [39], using elegant ion mobility measurements, have determined that, when $TiCl_4$ is ionized with 50 eV electrons, all of the Ti^+ ions formed are in excited states: 45% in the $a\ ^4F$ state (0.7 kcal/mol), 41% in the $a\ ^2F$ state (14 kcal/mol), and 14% in either the $a\ ^2D$ state (25 kcal/mol), the $b\ ^4P$ state (28.5 kcal/mol) or some combination of the two. Depending on how the 14% is distributed between these high energy states, these results would lead to an average electronic energy of between 9 and 10 kcal/mol for Ti^+, with states higher than 28 kcal/mol above the ground state being populated. Thus, for the $TiCl_4$ system, both excited atomic and molecular ions appear to be formed upon electron impact ionization.

Based on these considerations, we will assume that both sets of measurements can be correct, and all of the chlorotitanium cations could be formed with substantial internal energies. The "apparent BDEs" measured in this work are different than the ground state BDEs, and presumably can affect the chemistry of these ions.

4. Conclusions

The gas phase ion chemistry of the $TiCl_n^+$ ions from $TiCl_4$ with organic molecules continues to be one of the richest reactive systems studied using mass spectrometry [24]. The BDEs obtained for the successive loss of Cl atoms from $TiCl_4^+$ are clearly different from the thermochemical data obtained by KDD in a very different experiment. If the differences represent average internal energies, then they are not unreasonable in light of the unimolecular fragmentation of $TiCl_4$ following 70 eV ionization. The collection of information—mass spectra, KDD data, and internal energies reported here—yield an overall description of the 70 eV EI process for $TiCl_4$. The internal energies deposited (above the ionization energy) have a distribution that has a maximimum at approximately 5 eV, and extends out past 12 eV. Similar descriptions have been extracted from experimental data for organic molecules [36–38].

Information on internal energy content is useful for the evaluation of gas phase chemistry, both for endothermic and exothermic processes [40]. How can the likely presence of internal energy in these ions be further tested? There are at least three possibilities. The first is to attempt to measure changes in the reactivity of the various $TiCl_n^+$ ions as a function of the electron energies used to form the ions. Such studies appear to work best when the total number of atoms involved is small, such as in $\{M^+ + D_2 \rightarrow \text{products}\}$. In more complex systems characterized to date, such as $\{TiCl_3^+ + C_nH_{2n} \rightarrow \text{products}\}$, excess energy may be distributed/randomized through many degrees of freedom in the collision complex. In the reactions of atomic metal ions with organic molecules, this is frequently cited as a reason for not considering the influence of M^+ excited states in the gas phase ion/molecule reactions. If the reactant neutral is sufficiently large, ground and excited states tend to yield the same products. Whether this would occur for the $TiCl_n^+$ ions or not remains to be studied.

Another possible approach would be to determine if the BDEs reported here are sensitive to ionizing electron energy. Relative intensities of the ions in the mass spectrum change little in the 70–30 eV range, although ionization cross sections decrease, so the intensities of the ions under study would be much smaller than those used to obtain the data presented here. However, it is a basic premise of the EI process that energy content increases at electron energies above threshold, so that ionized molecules can yield fragments, which can then form subsequent fragment ions, etc. The sequential fragmentation following ionization suggested by the clastogram for $TiCl_4$ implies that this must be the case. The mapping of BDE versus ionizing electron energy for the set of ions discussed here is a substantial project, one that will not be pursued here.

A third possibility for investigating the presence of excess energy is to thermalize the ions following EI and measure their BDEs via their CID behavior. The MSU instrument is currently not capable of performing these experiments, but such measurements would provide the most direct measurement to determine if thermalized ions yield the BDEs suggested by KDD. We note that such experiments may be difficult to perform. While a variety of metal ions in a variety of states have been successfully thermalized collisionally, it appears to be difficult to do so for Ti^+. Whether this would be true for Ti-containing ions as well remains to be seen.

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